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FUNGICIDAL N-SUBSTITUTED AMIDES

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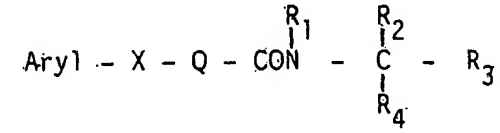
(57) Claim

1. A method of preventing or combatting Piricularia in rice plants which comprises the application to said plant of an effective amount of one or more compounds of formula (I)



(I)

in which

Aryl represents a phenyl group, either unsubstituted or mono- to tri-substituted by C_{1-5} alkyl groups, C_{1-5} alkoxy groups, C_{1-5} alkyl-SO_n groups wherein n represents one of the integers 0, 1 or 2, halogen atoms, groups of formula NO_2, CF_3, CN, CH_3OCH_2, $(CH_3)_2NCH_2$, COOalkyl, $CONH_2$ or phenyl groups; a 1- or

.../2

2-naphthyl group; an optionally chlorine-substituted 2-, 3- or 4-pyridyl group; or a pyrimidyl or quinolyl group;

Q represents a group of formula $-\overset{\overset{R_6}{|}}{\underset{\underset{R_5}{|}}{C}} - (CH_2)_m$

wherein m is one of the integers 0, 1 and 2;

R_1 represents a hydrogen atom or a C_{1-5} alkyl group or an allyl group,

R_2 and R_3 independently represent hydrogen atoms, C_{1-6} alkyl groups (which may also contain an O or S atom in the chain), C_{3-7} cycloalkyl groups, phenyl groups or groups of formula $CH_2\text{-}COO\text{-}(C_{1-5}$ alkyl); or R_2 and R_3 together represent a group of formula $-(CH_2)_4-$, $-(CH_2)_5-$, or $-\underset{\underset{CH_3}{|}}{CH}-(CH_2)_4-$;

R_4 represent a group of formula CN or $CONH_2$;

R_5 represents a hydrogen atom or a group of formula CH_3 or C_2H_5;

R_6 represents a hydrogen atom or a group of formula CH_3; and

X represents an oxygen or sulphur atom;

optionally in the form of racemates or mixtures of the optical isomers or in the form of the pure enantiomers or diast. eomers.

2. Compounds of formula (I)

$$\text{Aryl} - X - Q - CON - \overset{\overset{CH_3}{|}}{\underset{\underset{CN}{|}}{C}} - CH(CH_3)_2 \qquad (I)$$

wherein

Aryl represents a phenyl group, either unsubstituted or mono- to tri-substituted by C_{1-5} alkyl groups, C_{1-5} alkoxy groups, C_{1-5} alkyl-SO_n groups wherein n represents one of the integers 0, 1 or 2, halogen atoms, groups of formula NO_2, CF_3, CN, CH_3OCH_2, $(CH_3)_2NCH_2$, COOalkyl, $CONH_2$ or phenyl groups; a 1- or 2-naphthyl group; an optionally chlorine-substituted 2-, 3- or 4-pyridyl group; or a pyrimidyl or quinolyl group;

Q represents a group of formula $-\overset{\overset{R_6}{|}}{\underset{\underset{R_5}{|}}{C}} - (CH_2)_m$

wherein m is one of the integers 0, 1 and 2;

R_5 represents a hydrogen atom or a group of formula CH_3 or C_2H_5;

R_6 represents a hydrogen atom or a group of formula CH_3; and

X represents an oxygen or sulphur atom;

optionally in the form of racemates or mixtures of the optical isomers or

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Form 10

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Complete Specification for the invention entitled: "ARYLCARBOXYLIC ACID DERIVATIVES, THE PREPARATION AND USE THEREOF".

The following statement is a full description of this invention, including the best method of performing it known to me:—*

* Note: The description is to be typed in double spacing, pica type face, in an area not exceeding 250 mm in depth and 160 mm in width, on tough white paper of good quality and it is to be inserted inside this form.

Arylcarboxylic acid derivatives, the preparation and use thereof

The invention relates to compositions for combatting phytopathogenic fungi, active substances for these compositions and processes for preparing the active substances.

According to a first embodiment of the present invention, there is provided a method of preventing or combatting Piricularia in rice plants which comprises the application to said plants of an effective amount of one or more compounds of formula (I)

$$\text{Aryl} - X - Q - CON(R_1) - C(R_2)(R_4) - R_3 \qquad (I)$$

in which

Aryl represents a phenyl group, either unsubstituted or mono- to tri-substituted by C_{1-5} alkyl groups, C_{1-5} alkoxy groups, C_{1-5} alkyl-SO_n groups wherein n represents one of the integers 0, 1 or 2, halogen atoms, groups of formula NO_2, CF_3, CN, CH_3OCH_2, $(CH_3)_2NCH_2$, COOalkyl, $CONH_2$ or phenyl groups; a 1- or 2-naphthyl group; an optionally chlorine-substituted 2-, 3- or 4-pyridyl group; or a pyrimidyl or quinolyl group;

Q represents a group of formula $-C(R_6)(R_5)-(CH_2)_m$

wherein m is one of the integers 0, 1 and 2;

R_1 represents a hydrogen atom or a C_{1-5} alkyl group or an allyl group,

R_2 and R_3 independently represent hydrogen atoms, C_{1-6} alkyl groups (which may also contain an O or S atom in the chain), C_{3-7} cycloalkyl groups, phenyl groups or groups of formula CH_2-COO-(C_{1-5} alkyl); or

R_2 and R_3 together represent a group of formula $-(CH_2)_4-$, $-(CH_2)_5-$, or $-CH(CH_3)-(CH_2)_4-$;

R_4 represent a group of formula CN or $CONH_2$;

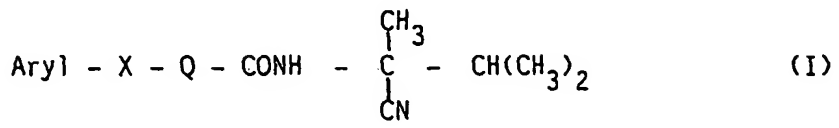
R_5 represents a hydrogen atom or a group of formula CH_3 or C_2H_5;

R_6 represents a hydrogen atom or a group of formula CH_3; and

X represents an oxygen or sulphur atom;

optionally in the form of racemates or mixtures of the optical isomers or in the form of the pure enantiomers or diastereomers.

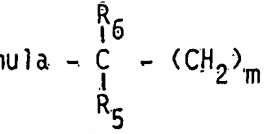
According to a second embodiment of the present invention there is provided compounds of formula (I)



(I)

wherein

Aryl represents a phenyl group, either unsubstituted or mono- to tri-substituted by C_{1-5} alkyl groups, C_{1-5} alkoxy groups, C_{1-5} alkyl-SO_n groups wherein n represents one of the integers 0, 1 or 2, halogen atoms, groups of formula NO_2, CF_3, CN, CH_3OCH_2, $(CH_3)_2NCH_2$, COOalkyl, $CONH_2$ or phenyl groups; a 1- or 2-naphthyl group; an optionally chlorine-substituted 2-, 3- or 4-pyridyl group; or a pyrimidyl or quinolyl group;

Q represents a group of formula 

wherein m is one of the integers 0, 1 and 2;

R_5 represents a hydrogen atom or a group of formula CH_3 or C_2H_5;

R_6 represents a hydrogen atom or a group of formula CH_3; and

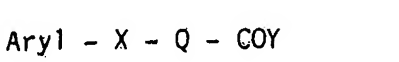
X represents an oxygen or sulphur atom;

optionally in the form of racemates or mixtures of the optical isomers or in the form of the pure enantiomers or diastereomers.

According to a third embodiment of the present invention there is provided a fungicidal composition comprising a compound as described in the second embodiment optionally in the form of racemates or mixtures of the optical isomers or in the form of the pure enantiomers or diastereomers, together with excipients and/or carriers.

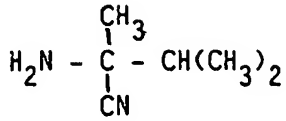
According to a fourth embodiment of the present invention there is provided a process for preparing compounds of formula (I) as described in the second embodiment wherein

(a) a compound of formula (II)



(II)

wherein Aryl, X and Q are as described in the second embodiment and Y represents a leaving group, is reacted with a compound of formula (III)



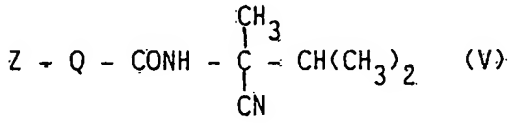
(III)

or

b) a compound of formula (IV)

(IV)

wherein Aryl and X are as described in the second embodiment and M represents a hydrogen atom or an alkali metal cation, is reacted with a compound of formula (V)



(V)

wherein Q is as described inthe second embodiment and Z represents a halogen atom or an arylsulphonyloxy group,

and, if desired, mixtures of enantiomers obtained are separated by conventional methods into the individual enantiomers or into pairs of diastereomers.

The compounds of formula I may contain asymmetric carbon atoms and the invention includes the individual enantiomers of such compounds and also mixtures thereof.

In the substituents R_1 to R_6 contain hydrocarbon chains, these may be straight or branched and may be identical to or different from one another. Chains with up to 4, more particularly up to 3 carbon atoms are preferred. The preferred alkyl substituent in the aryl group is a methyl group. Halogen atoms include fluorine, chlorine, bromine and iodine, preferably chlorine or fluorine. The substituents in the aryl group may be identical or different although the groups of formulae CF_3, CN, NO_2, $(CH_3)_2NCH_2$ and C_{1-5} alkyl-SO_n and the phenyl group generally occur only once. If aryl

represents a quinolinyl group it is preferably an 8-quinolinyl group.

The compounds of formula (I) may be prepared by several processes and these processes from a still further feature of the invention. These processes include:

1. reaction of a compound of formula (II)

$$\text{Aryl} - X - Q - COY \qquad \text{(II)}$$

wherein aryl, X and Q are as hereinbefore defined and Y represents a leaving group, e.g. a halogen atom (preferably chlorine), or an alkoxy, hydroxy or acyl group, with a compound of formula (III)

$$HN(R_1) - C(R_2)(R_4) - R_3 \qquad \text{(III)}$$

wherein R_1 - R_4 are as hereinbefore defined, thereby eliminating HY; and

2. reaction of a compound of formula (IV)

$$\text{Aryl} - XM \qquad \text{(IV)}$$

wherein aryl and X are as hereinbefore defined and M indicates a hydrogen atom or an alkali metal cation, with a compound of formula (V)

$$Z - Q - CON(R_1) - C(R_2)(R_4) - R_3 \qquad \text{(V)}$$

wherein R_1 to R_4 and Q are as hereinbefore defined and Z represents a halogen atom or an arylsulphonyloxy group.

The reaction of type (1) is preferably carried out in an inert solvent, e.g. methylene chloride, toluene, acetonitrile, an ether, or in a mixture of solvents at temperatures between ambient temperature and the boiling temperature of the reaction mixture; the reaction will be promoted if an HY-binding agent is present, for example a base if HY represents an acid such as HCl, or dicyclohexylcarbodiimide or carbonyldiimidazole if HY represents water.

The starting materials of formula (II) are known compounds or may easily be prepared by conventional methods. Thus compounds of formula (II) wherein Y = OH may be obtained for example by reaction of a suitable phenol or thiophenol (aryl-XH) with an ester of a suitable bromosubstituted carboxylic acid in the presence of a base and subsequent hydrolysis of the ester. From the carboxylic acids thus obtained, the corresponding carboxylic acid chlorides of formula (II) are formed, e.g. by reacting with thionyl chloride.

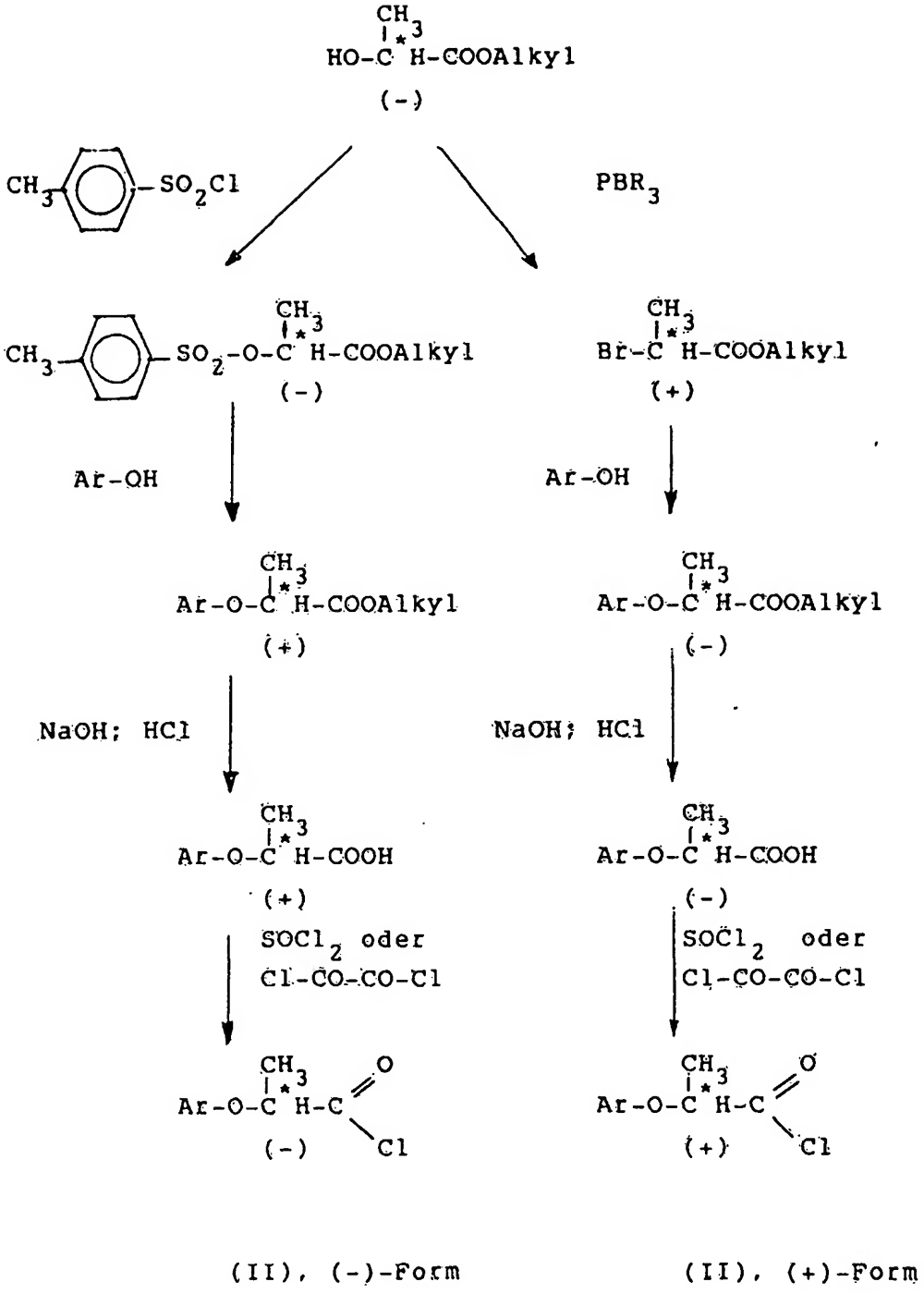
The α-amino acid nitriles (compounds of formula (II) wherein R_4 = CN), may be prepared by Strecker synthesis from the corresponding ketone or aldehyde, NaCN and NH_4Cl in water (see Houben-Weyl, Vol. VIII, page 274ff (1952)). The α-amino acid amides (compounds of formula (III) wherein R_4 = $CONH_2$) are obtained from the corresponding nitriles by partial hydrolysis.

The reaction of type (2) may be carried out in an inert polar solvent. If M = H, a base is desirably added. Conditions under which a compound of formula (IV) wherein M = K or Na is formed are preferred.

The preferred definitions of Z in formula (V) are a bromine atom or a group of formula $CH_3-C_6H_4-SO_3-$ whilst the preferred solvent is acetonitrile. The reaction is generally carried out at elevated temperatures, e.g. at reflux temperature. Suitable bases include, for example, alkali metal carbonates, alkali metal hydroxides, and optionally also sufficiently basic amines such as triethylamine.

Depending on the definitions of R_2 to R_6, compounds of formula I with one or two centres of asymmetry may occur. The isomers may, if desired, be separated by conventional methods or synthesised directly by using optically active starting products.

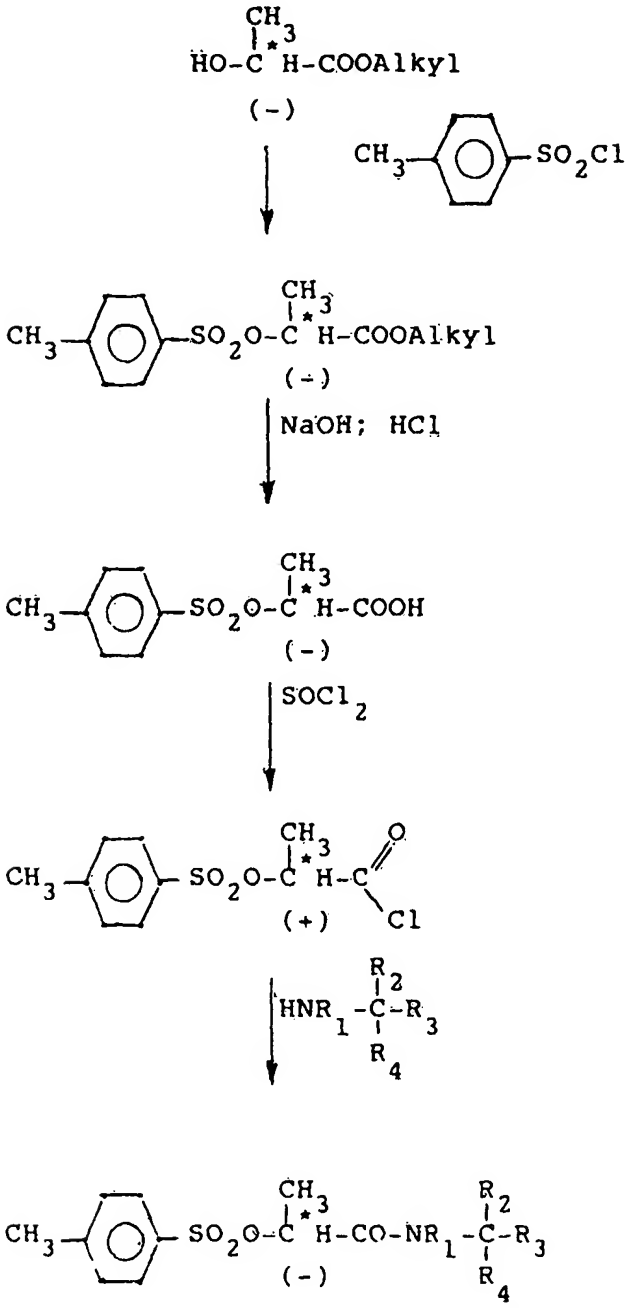
Two methods of preparing optically active compounds of formula (II) from an optically active α-hydroxy acid ester are illustrated below (the asymmetric carbon is marked with an asterisk):



(II), (-)-Form (II), (+)-Form

"Alkyl" preferably represents methyl or ethyl. Other compounds of formula (II) may be prepared according to the same general scheme.

Similar steps lead to optically active starting materials of formula (V); in this case, too, other optically active compounds of formula (V) may be obtained accordingly.



(V), (-)-Form

The compounds of formula I have a fungitoxic effect on phytopathogenic fungi, and accordingly methods of preventing and/or combating fungal infections in plants form a yet further feature of the invention. The compounds may be used particularly against fungal diseases in rice, for instance Piricularia.

Although the new compounds are partly derived from herbicides (Dichlorprop, 2,4-DB) they are surprisingly well tolerated by plants.

To prepare the fungicidal compositions according to the invention the compounds of formula (I) are processed with conventional excipients and/or carriers to produce the usual preparations, which may be diluted for use in the form of a spray liquor with suitable quantities of water. Preparations of this kind include, for example, emulsifiable and soluble concentrates, wettable powders, dusting powders and granules which may contain up to 80% by weight of active substance.

The activity of the compounds according to the invention, e.g. against Piricularia, was tested on rice seed under tropical conditions. 2 rows of rice seed (I and II) between older rows naturally infected with Piricularia were treated on the 41st, 45th and 49th day after sowing with spray liquors containing specific quantities of active substance. A control treated only with water was used as a comparison. The results were graded 6, 8, 10 and 13 days after the last spraying (expressed as a % of plants attacked).

The compounds according to the invention proved highly effective against Piricularia and well tolerated by the plants.

Additional tests are described hereinafter.

Effect against Piricularia in rice

A. Leaf treatment

Rice plants were first grown in propagation trays. They were sprayed until dripping wet with emulsions or suspensions containing 1000, 500 or 250 ppm of the active substance in question. Two days after treatment the propagation trays were left in the open between infected rice plants for 5-6 days to allow infection to occur. Findings were evaluated 5-8 days later.

B. Soil treatment

Rice plants were first grown in flower pots. Emulsions or suspensions containing 500 ppm of the active substances specified were poured onto the roots. Two days after treatment the pots were left in the open for 4-6 days between rice plants infected with Piricularia in order to allow infection to occur. The results were evaluated 5-7 days after the infection.

The findings were graded 1 to 3:

1: no attack
2: slight attack
3: attack similar to that of the untreated control.

The numbers given in Table A hereinafter are averages from 3 tests and several grades awarded at different times.

C. Application under water (submerged application)

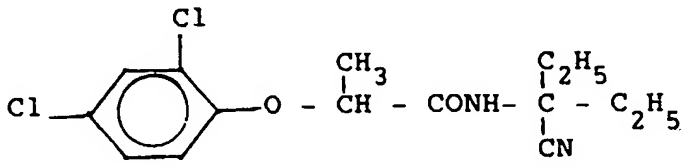
Rice plants were planted in earth-filled buckets. Water was added until it formed an unbroken covering over the earth. A quantity of active substance was added in the form of a suspension or emulsion to correspond to an application of 8 or 4 or 2 kg/ha active ingredient. Two days after treatment the test plants were left in the open between infested rice plants and remained exposed to infection throughout the experiment. The results were evaluated one day after attack had occurred on the untreated control and the evaluation was carried out 4-5 times (3 experiments with each substance). Evaluation was as in A and B. The numbers in the table are the averages from three experiments and several grades awarded at different times as the experiment progressed.

Table A: Test results

Active substance according to Example:	Concentration of active substance [ppm]	Number of attacks Test A	Test B	Test C kg/ha	Test C Number of Attacks
Tab. II No. 62	1000 500 250	1.0 1.0 1.0	1.8	8	2.0
Example No. 9	1000 500 250	1.0 1.0 1.5	2.0	4 2	1.8 2.2
Tab. II No. 1	1000 500 250	- 1.0 1.0	2.5	8	1.8
Tab. V No. 2	1000 500 250	1.0 1.5 2.5	1.0	4	1.5
Example No. 4	1000 500 250	1.0 1.8 2.1	2.1	8	1.8
Tab. II No. 2	1000 500 250	1.1 1.0 2.0	-	4	2.0
Tab. II No. 33	1000 500 250	1.0 1.0 2.0	-		
Example No. 6e	1000 500 250	1.5 2.0 2.0	2.0		
Tab. IV No. 6	1000 500 250	- 1.0 1.0	1.9		

Example 1

2-(2,4-Dichlorophenoxy)-propionic acid-N-(1-ethyl-1-cyanopropyl)-amide



2.2 g of 3-amino-3-cyanopentane and 2.4 g of triethylamine are dissolved in 100 ml of methylene chloride. 5.1 g of 2-(2,4-dichlorophenoxy)-propionic acid chloride are added and the mixture is stirred overnight at ambient temperature. The solution is extracted with water and sodium hydrogen carbonate solution, dried and evaporated down. The residue obtained consists of 6.3 g (96% of theory) of a brownish viscous oil which crystallizes when stirred with diisopropylether.

Yield: 4.9 g of white solids (74% of theory)
Melting point: 100 - 102°C

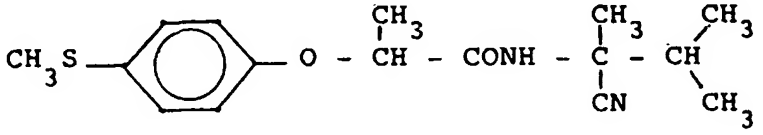
The structure is confirmed by spectroscopic investigation.

Analysis: $C_{15}H_{18}Cl_2N_2O_2$ M = 329.23

	C%	H%	Cl%	N%
Found:	54.58	5.54	21.06	8.35
Calculated:	54.72	5.51	21.54	8.51

Example 2

2-(4-Methylthiophenyloxy)-propionic acid-N-(1-cyano-1,2-dimethylpropyl)-amide



2.5 g of 2-bromopropionic acid-N-(1-cyano-1,2-dimethyl-propyl)-amide (prepared analogously to Example 5a) and 1.4 g of 4-methylmercaptophenol are dissolved in 50 ml of methylisobutylketone. After the addition of 1.5 g of potash the mixture is stirred for 3 hours at 80°C. The solution is suction filtered and evaporated down. 2.8 g of brownish oil are obtained (91.5%) which crystallises when stirred with diisopropylether.
M.p. 83-86°C

Analysis: $C_{16}H_{22}N_2O_2S$ M = 306.43

	C%	H%	N%	S%
Found:	62.48	7.24	9.23	10.34
Calculated:	62.71	7.24	9.14	10.46

The structure was confirmed by spectroscopy.

Example 3

2-(4-Chloro-2-methylphenoxy)-propionic acid-N-[3-cyanopent-3-yl]-amide

4.4 g of 2-amino-2-ethylbutyronitrile (0.039 mol) and 4.6 g of triethylamine (0.046 mol) are dissolved

in methylene chloride, 9.0 g of 2-(4-chloro-2-methyl-phenoxy)-propionic acid chloride (0.039 mol) are added dropwise with stirring. The mixture heats up. It is stirred for a further 3 hours without heating, extracted successively with water and bicarbonate solution, then dried and evaporated down. The residue obtained consists of a brown oil (10.8 g) which crystallises when stirred with isopropylether. The product is suction filtered and dried.

Yield: 10.6 g (88% of theory) of white solids
M.p.: 125 - 126°C.

Elemental analysis and NMR spectrum confirm the formula given.

Example 4

2-(4-Chloro-2-methylphenoxy)-propionic acid-N-[2-cyano-3-methylbut-2-yl]-amide

Analogously to Example 3 the title compound is obtained from equimolar quantities of 2-amino-2,3-dimethylbutyronitrile.

Yield: 76% of theory; m.p.: 97 - 99°C.

The product is initially obtained as a brown oil. It consists of 4 isomers. The mixture can be resolved into 3 fractions by step-wise precipitation with cold ether.

From 11.1 g of oil are obtained:

Fraction I: 1.8 g of white solids
m.p.: 117-118°C;

Fraction II: 1.8 g of brownish solids
m.p.: 94-96°C;
Fraction III: 5.6 g of reddish oil (purified by chromatography)

NMR spectroscopy indicates enrichment of the pairs of enantiomers in Fractions I and II:

Fraction I	Enantiomeric pair I to enantiomeric pair II 89 : 11 (diastereomeric ratio)
Fraction II	Enantiomeric pair I to enantiomeric pair II 26 : 74

The pairs of enantiomers may be further concentrated by recrystallising the fractions.

The following compounds of the general formula given below were also obtained in accordance with the preceding Examples:

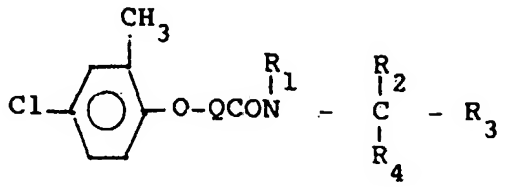


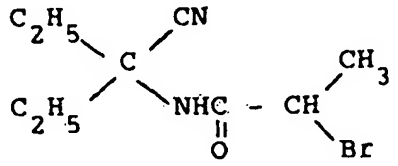
Table I

No.	Q	R_2	R_3	R_1	R_4	Mp. [°C]
1	CH_2	C_2H_5	C_2H_5	H	CN	86-88
2	$CH(CH_3)$	$i\text{-}C_3H_7$	CH_3	H	$CONH_2$	108-111
3	CH_2	$i\text{-}C_3H_7$	CH_3	H	$CONH_2$	105-107
4	CH_2	$i\text{-}C_3H_7$	CH_3	H	CN	102-103
5	$CH(CH_3)$	$n\text{-}C_3H_7$	CH_3	H	CN	71-75
6	$CH(CH_3)$	C_2H_5	CH_3	H	CN	86-87
7	$CH(CH_3)$	$n\text{-}C_3H_7$	CH_3	H	$CONH_2$	100-102
8	$CH(CH_3)$	$n\text{-}C_5H_{11}$	CH_3	H	CN	
9	$CH(CH_3)$	$-(CH_2)_5-$		H	CN	134-136
10	CH_2	$-(CH_2)_5$		H	CN	118-120
11	CH_2	$i\text{-}C_3H_7$	CH_3	CH_3	CN	
12	$CH(CH_3)$	$i\text{-}C_3H_7$	CH_3	CH_3	CN	Oil
13	$CH(CH_3$	$-(CH_2)_4-$		H	CN	143-146
14	$CH(CH_3)$	$-CH(CH_3)-(CH_2)_4$		H	CN	121-127

Example 5

2-(4-Chlorophenylthio)-propionic acid-N-(1-ethyl-1-cyanopropyl)-amide

a) 2-Bromopropionic acid-N-(1-ethyl-1-cyanopropyl)-amide

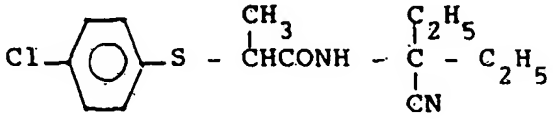


36.5 g of 2-amino-2-cyano-n-pentane in 100 ml of methylene chloride are added dropwise, with stirring, over a period of 40 minutes, to 88.4 g of 2-bromopropionic acid anhydride (0.325 mol) dissolved in 280 ml of methylene chloride. After stirring overnight, the solution is extracted with water and sodium bicarbonate solution, dried and evaporated down. The remaining oil is triturated with a little ether whereupon the product crystallises out.

M.p. 85-87°C

Yield: 61.2 g (76.5% of theory)

b)



5.8 g of 4-chlorothiophenol (0.04 mol) are stirred in 150 ml of methylisobutylketone with 12.2 g of potassium carbonate at 90°C for 10 minutes. 9.9 g of 2-bromopropionic acid-N-(1-ethyl-1-

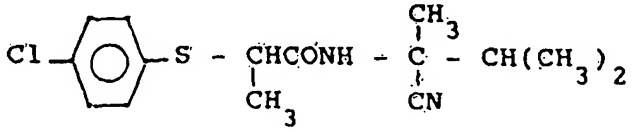
cyanopropyl)-amide are added to the resulting suspension with stirring and the mixture is stirred for another 5 hours at about 90°C. The solution is filtered, extracted successively with water, 2N sodium hydroxide solution and water, dried with magnesium sulphate and evaporated down. A brown oil is obtained which hardens to form a brownish crystalline mass when stirred with a little ether.

M.p. 108-110°C
Yield: 7.2 g (58.1% of theory)

Elemental analysis

	C	H	N	Cl	S
Calc.:	57.96%	6.16%	9.01%	11.4%	10.32%
Found:	57.77%	6.35%	8.86%	11.32%	10.28%

The following compound is also obtained according to the preceding Example



M.p.: 106-109°C.

Example 6

(+)-2-(4-Chloro-2-methylphenoxy)-propionic acid-N-(1-ethyl-1-cyanopropyl)-amide

a) Methyl (-)-O-(4-methylphenylsulphonyl)-lactate

26.9 g of triethylamine are added dropwise to a solution of 25.2 g of methyl S-(-)-lactate and 46.1 g of p-toluenesulphonic acid chloride

in 160 ml of toluene. The mixture is stirred overnight and the precipitate is removed by suction filtering. The toluene solution is extracted with dilute hydrochloric acid and water, dried with sodium sulphate and evaporated down. 55.9 g of colourless oil are obtained, which is purified by vacuum distillation.
B.p.$_{0.2}$: 148-152°C $[\alpha]_D^{24}$: -50.1° (ethanol)
Yield: 43.5 g (70% of theory)

b) Methyl (+)-(4-chloro-2-methylphenoxy)-propionate

41.9 g of methyl S-(-)-O-(4-methylsulphonyl)-lactate and 23.1 g of 4-chloro-2-methylphenol are dissolved in 100 ml of acetonitrile, 50 g of potash are added and the mixture is refluxed for 10 hours with stirring. The solution is suction filtered and evaporated down. The residue is taken up in toluene, extracted with 1N sodium hydroxide solution, dried and concentrated by evaporation. 32.2 g of reddish liquid are obtained (87% of theory)

c) (+)-4-Chloro-2-methylphenoxypropionic acid

The crude product obtained in b) (32.2 g) is dissolved in 100 ml of acetone. A solution of 6.8 g of NaOH in 30 ml of water is added dropwise with stirring and while cooling with ice. After stirring overnight the mixture is diluted with water and extracted with methylene chloride. The aqueous solution is acidified with conc. hydrochloric acid and the product precipitated is extracted with methylene chloride. The methylene chloride solution is separated off, dried and evaporated down. An oily residue is obtained which solidifies immediately.

M.p.: 62-72°C (pressed onto clay)
$[\alpha]_D^{24}$: + 14.1° (ethanol)
Yield: 27.7 g (91% of theory)

d) (-)-4-Chloro-2-methylphenoxypropionic acid chloride

27.2 g of (+)-4-chloro-2-methylphenoxypropionic acid and 30.2 g of thionyl chloride are stirred with 100 ml of toluene for 3 hours at 100°C. The solution is evaporated down in vacuo. 29.6 g of brown oil are obtained, which is reacted without purification.

e) (+)-2-(4-Chloro-2-methylphenoxy)-propionic acid-N-(1-ethyl-1-cyanopropyl)-amide

8.4 g of the crude product from d) are added dropwise to 4 g of 3-amino-3-cyano-n-pentane and 4.4 g of triethylamine, dissolved in 100 ml of toluene, at -20 to -30°C with stirring. The mixture is then stirred for 3 hours at RT, extracted with water and the solution is evaporated down. The oily residue (8.8 g) is stirred with diisopropylether, whereupon a crystalline product is precipitated and then separated off.
Yield: 2.8 g (25% of theory)
M.p.: 98-100°C
$[\alpha]_D^{22}$: + 9.1° (ethanol)

Example 7

(-)-2-(4-Chloro-2-methylylphenoxy)-propionic acid-N-(1-ethyl-1-cyanopropyl)-amide

a) Ethyl (+)-2-bromopropionate

47.2 g of ethyl S-(-)-lactate are dissolved in 300 ml of methylene chloride. 108 g of phosphorus tribromide are added dropwise. The reaction is exothermic. After stirring overnight at RT the mixture is poured onto ice and stirred with water. The methylene chloride solution is extracted with bicarbonate solution, dried and evaporated down. The residue is distilled. Yield: 33.8 g; colourless oil (47% of theory) $Bp_{25\ mbar}$ 55-56°C.

b) Ethyl (-)-(4-chloro-2-methylphenoxy)-propionate

The product described in a) (33.8 g) is dissolved together with 26.7 g of 4-chloro-2-methylphenol in 300 ml of toluene and after the addition of 52 g of K_2CO_3 it is refluxed for 10 hours with stirring. The solution is suction filtered, extracted twice with 1N sodium hydroxide solution, dried and evaporated down. 34.3 g of clear liquid are obtained (76% of theory)
$[\alpha]_D^{22}$: -14.46° (ethanol)

c) (-)-(4-Chloro-2-methylphenoxy)-propionic acid ((-)-CMPP)

Hydrolysis of the ester obtained in b) is carried out as in Example 6c).

From 24.2 g of ethyl (-)-(4-chloro-2-methylphenoxy)-propionate, 19.7 g of (-)-(4-chloro-2-methylphenoxy)-propionic acid are obtained (92% of theory).

M.p.: 69-75°C
$[\alpha]_D^{22}$: -9.679° (ethanol)

d) (+)-(4-Chloro-2-methylphenoxy)-propionic acid chloride
((+)-CMPP-chloride)
The acid described in 7c) is converted analogously to Example 6d) into the acid chloride which is further processed without purification.
From 8.6 g of (-)-CMPP, 8.4 g of (+)-CMPP chloride is obtained as a brownish oil (90% of theory)
$[\alpha]_D^{22}$: +4.486° (CCl_4)

e) (-)-2-(4-Chloro-2-methylphenoxy)-propionic acid-N-(1-ethyl-1-cyanopropyl)-amide

The (+)-CMPP chloride is reacted with 3-amino-3-cyano-n-pentane as described in Example 6e). 3 g of (-)-2-(4-chloro-2-methylphenoxy)-propionic acid-N-(1-ethyl-1-cyanopropyl)-amide are obtained (28% of theory) from 8 g of (+)-CMPP chloride.
M.p.: 98-100°C
$[\alpha]_D^{22}$: -8.584° (ethanol)

A variant for the preparation of the dextrorotatory phenoxypropionic acid amides is described hereinafter taking as an example (+)-2-(4-chloro-2-methylphenoxy)-propionic acid-N-(1-ethyl-1-cyanopropyl)-amide:

Example 8

(+)-2-(4-Chloro-2-methylphenoxy)-propionic acid-N-(1-ethyl-1-cyanopropyl)-amide

a) (+)-O-(4-Methylphenylsulphonyl)-lactic acid chloride

17.9 g of (-)-O-(4-methylphenylsulphonyl)-lactic acid (Helv. Chim. Acta 65/1240 (1982)) and 13 g of thionyl chloride are stirred at 95-100°C for 3 hours. The product is evaporated down in vacuo and degassed. 19.2 g of brown oil are obtained (100% of theory).

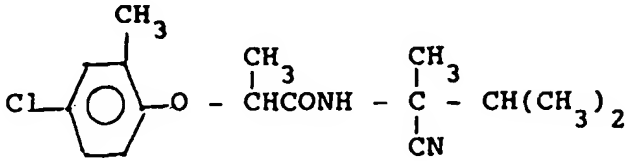
b) (-)-O-(4-Methylsulphonyl)-lactic acid-N-(1-ethyl-1-cyanopropyl)-amide

18.8 g of the crude product from 8a) are added dropwise at -20 to -30°C to a solution of 8 g of 3-amino-3-cyano-n-pentane and 8.8 g of triethylamine in 200 ml of toluene. The mixture is stirred for 3 hours at -20°C and then overnight at RT. The solution is extracted with water and evaporated down. 23.4 g of brown clear oil are obtained (96% of theory) which is crystallised by stirring with diisopropylether.
M.p.: 57-60°C $[\alpha]_D^{22}$ -40.4° (ethanol)
Yield: 8.4 g (34% of theory)

c) (+)-2-(4-Chloro-2-methylphenoxy)-propionic acid-N-(1-ethyl-1-cyanopropyl)-amide

4.7 g of (-)-O-(4-methylsulphonyl)-lactic acid N-(1-ethyl-1-cyanopropyl)-amide and 2 g of 4-chloro-2-methylphenol are dissolved in 100 ml of toluene. 4.5 g of powdered potash are added and the mixture is refluxed for 12 hours with stirring. The solution is suction filtered, extracted with 1N sodium hydroxide solution and evaporated down. 3.1 g of yellow oil are obtained (72% of theory) which crystallises when stirred with diisopropylether. 2.2 g of white crystalline solids are obtained (51% of theory).
M.p.: 97-99°C $[\alpha]_D^{22}$: +11.94° (ethanol)

In accordance with Examples 6 to 8, the dextro- and levorotatory enantiomers of the following compound are also prepared:



Example 9: $[\alpha]_D^{22} = 9.1°$ (ethanol) oils, mixtures of diastereomers

Example 10: $[\alpha]_D^{22} = -7.65°$ (ethanol)

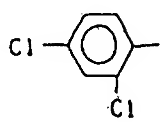
The following compounds, listed in Tables II to IX, were prepared by analagous methods.

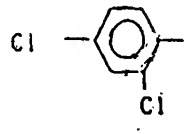
13.11.87 77667

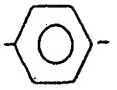
T A B L E I I

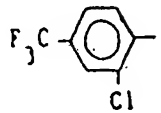
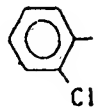
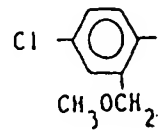
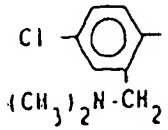
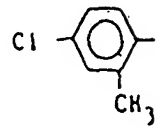
Compounds of formula

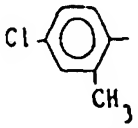
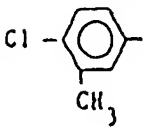
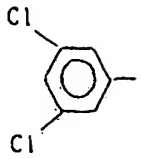
$$\text{Aryl} - O - \underset{R_6}{\overset{R_5}{\underset{|}{\overset{|}{C}}}} - CO - \overset{R_1}{\overset{|}{N}} - \underset{R_4}{\overset{R_2}{\underset{|}{\overset{|}{C}}}} - R_3$$

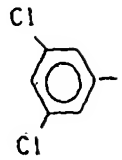
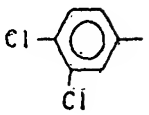
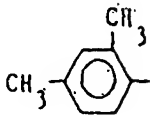
No.	Aryl	R_1	R_2	R_3	R_4	R_5	R_6	Mp (°C)
1		H	CH_3	$CH(CH_3)_2$	CN	H	CH_3	79-80
2	"	H	CH_3	C_2H_5	CN	H	CH_3	105-107
3	"	CH_3	CH_3	$CH(CH_3)_2$	CN	H	CH_3	Oil
4	"	H	$-(CH_2)_5-$		CN	H	CH_3	142-144
5	"	H	CH_3	$n-C_5H_{11}$	CN	H	CH_3	65-67
6	"	H	CH_3	$CH_2CH_2CH(CH_3)_2$	CN	H	CH_3	74-76

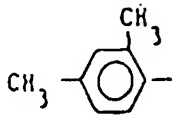
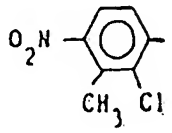
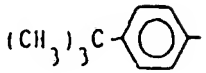
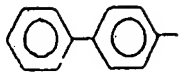
No.	Aryl	R_1	R_2	R_3	R_4	R_5	R_6	Mp (°C)
7		H	C_2H_5	$CH_2CH(CH_3)_2$	CN	H	CH_3	70-75
8	"	H	CH_3	$CH_2CH(CH_3)_2$	CN	H	CH_3	74-75
9	"	H	$-(CH_2)_4-$		CN	H	CH_3	117-119
10	"	H	H	$CH(CH_3)_2$	CN	H	CH_3	Oil
11	"	H	CH_3	$-CH_2OCH_3$	CN	H	CH_3	Oil
12	"	H	$-CH(CH_3)-(CH_2)_4-$		CN	H	CH_3	129-134
13	"	H	CH_3	$-CH_2COOC_2H_5$	CN	H	CH_3	

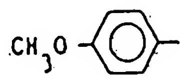
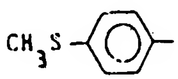
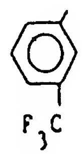
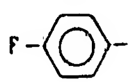
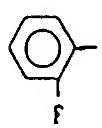
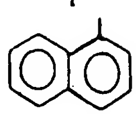
No.	Aryl	R_1	R_2	R_3	R_4	R_5	R_6	Mp (°C)
14		H	CH_3	$CH(CH_3)_2$	CN	H	H	85-87
15	"	H	$-(CH_2)_5-$		CN	H	H	94-96
16	"	H	C_2H_5	C_2H_5	CN	H	H	50-52
17	"	H	CH_3	$CH(CH_3)_2$	CN	H	CH_3	80-81
18	"	CH_3	CH_3	$CH(CH_3)_2$	CN	H	CH_3	Oil
19	"	H	C_2H_5	C_2H_5	CN	H	CH_3	83-84
20	"	H	CH_3	$n-C_5H_{11}$	CN	H	CH_3	75-77
21	"	H	CH_3	$CH_2CH(CH_3)_2$	CN	H	CH_3	58-62

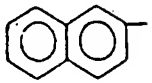
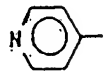
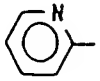
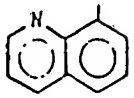
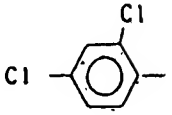
No.	Aryl	R_1	R_2	R_3	R_4	R_5	R_6	Mp (°C)
22	C_6H_5	H	CH_3	$CH(CH_3)_2$	CN	H	CH_3	81-83
23		H	CH_3	$CH(CH_3)_2$	CN	H	CH_3	120-124
24		H	CH_3	$CH(CH_3)_2$	CN	H	CH_3	60-62
25	"	H	CH_3	$n\text{-}C_5H_{11}$	CN	H	CH_3	97-100
26		H	CH_3	$CH(CH_3)_2$	CN	H	CH_3	Oil
27		H	CH_3	$CH(CH_3)_2$	CN	H	CH_3	Oil
28		H	CH_3	$CH(CH_3)_2$	CN	H	C_2H_5	98-100

No.	Aryl	R_1	R_2	R_3	R_4	R_5	R_6	Mp (°C)
29		H	CH_3	$CH(CH_3)_2$	CN	CH_3	CH_3	94-97
30		H	CH_3	$CH(CH_3)_2$	CN	H	CH_3	110
31	"	H	CH_3	$n\text{-}C_5H_{11}$	CN	H	CH_3	Oil
32	"	H	CH_3	$CH(CH_3)_3$	$CONH_2$	H	CH_3	155
33		H	CH_3	$CH(CH_3)_3$	CN	H	CH_3	105
34	"	H	CH_3	$CH(CH_3)_3$	$CONH_2$	H	CH_3	140

No.	Aryl	R_1	R_2	R_3	R_4	R_5	R_6	Mp (°C)
35		H	CH	$n-C_5H_{11}$	CN	H	CH_3	Oil
36		H	CH_3	$CH(CH_3)_2$	CN	H	CH_3	103
37	"	H	CH_3	$CH(CH_3)_2$	$CONH_2$	H	CH_3	150
38	"	H	CH_3	$n-C_5H_{11}$	CN	H	CH_3	Oil
39		H	CH_3	$CH(CH_3)_2$	CN	H	CH_3	106
40	"	H	CH_3	$n-C_3H_7$	CN	H	CH_3	142

No.	Aryl	R_1	R_2	R_3	R_4	R_5	R_6	Mp (°C)
41		H	C_2H_5	C_2H_5	CN	H	CH_3	114
42	"	H		$-(CH_2)_5-$	CN	H	CH_3	121
43	"	CH_3	CH_3	$CH(CH_3)_2$	$CONH_2$	H	CH_3	85-90
44		H	CH_3	$CH(CH_3)_2$	CN	H	CH_3	160
45	"	H	C_2H_5	C_2H_5	CN	H	CH_3	152-154
46		H	CH_3	$CH(CH_3)_2$	CN	H	CH_3	88-90
47		H	CH_3	$CH(CH_3)_2$	CN	H	CH_3	106-108

No.	Aryl	R_1	R_2	R_3	R_4	R_5	R_6	Mp (°C)
48		H	CH_3	$CH(CH_3)_2$	CN	H	CH_3	98-100
49		H	CH_3	$CH(CH_3)_2$	CN	H	CH_3	57-63
50		H	C_2H_5	C_2H_5	CN	H	CH_3	
51		H	CH_3	$CH(CH_3)_2$	CN	H	CH_3	78-81
52		H	CH_3	$CH(CH_3)_2$	CN	H	CH_3	72-75
53		H	CH_3	$CH(CH_3)_2$	CN	H	CH_3	98-102
54		H	CH_3	$CH(CH_3)_2$	CN	H	CH_3	152-57

No.	Aryl	R_1	R_2	R_3	R_4	R_5	R_6	Mp (°C)
55		H	CH_3	$CH(CH_3)_2$	CN	H	CH_3	90-95
56		H	CH_3	$CH(CH_3)_2$	CN	H	CH_3	
57		H	CH_3	$CH(CH_3)_2$	CN	H	CH_3	80
58		H	CH_3	$CH(CH_3)_2$	CN	H	CH_3	125-128
59		H	CH_3	$CH(CH_3)_2$	CN	H	CH_3	105-107
60	"	H	CH_3	$CH_2CH(CH_3)_2$	CN	H	CH_3	
61		H	$CH(CH_3)_2$	$CH(CH_3)_2$	CN	H	CH_3	82-84

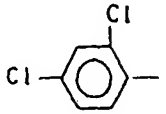
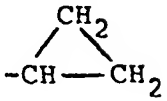
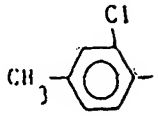
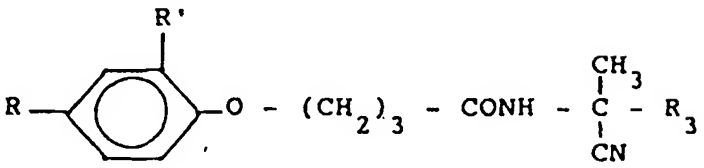
No.	Aryl	R_1	R_2	R_3	R_4	R_5	R_6	Mp (°C)
62		H	CH_3		CN	H	CH_3	89-94
63	"	H	CH_3	$-CH(SCH_3)-CH_3$	CN	H	CH_3	124-128
64	"	H	CH_3	$CH_2-COOC_2H_5$	CN	H	CH_3	
65	"	H	CH_3	$-CH(CH_3)-C_2H_5$	CN	H	CH_3	107-110
66		H	CH_3	$CH(CH_3)_2$	CN	H	CH_3	

TABLE III

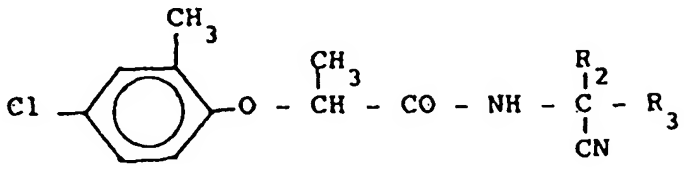
Compounds of formula



No.	R_3	R	R'	Mp.(°C)
1	$CH(CH_3)_2$	Cl	CH_3	Oil
2	$n\text{-}C_5H_{11}$	Cl	CH_3	Oil
3	$CH(CH_3)_2$	CH_3	Cl	
4	$n\text{-}C_5H_{11}$	CH_3	Cl	

Table IV

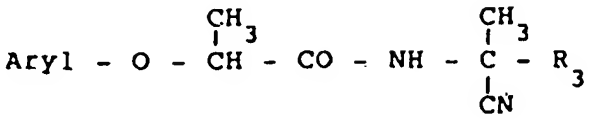
Compounds of formula

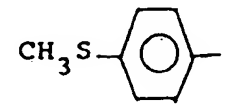
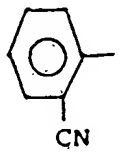
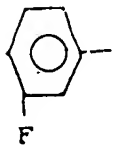
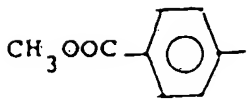
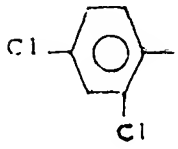


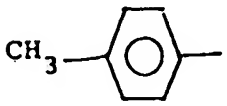
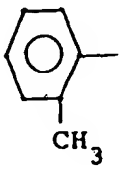
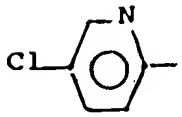
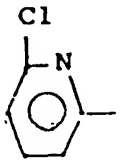
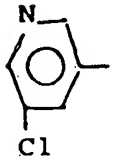
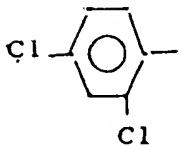
NO.	R_2	R_3	M p. [°C]
1	CH_3	$n\text{-}C_3H_7$	71-75
2	CH_3	C_2H_5	86-87
3	C_2H_5	C_2H_5	125-126
4	CH_3	$CH_2CH(CH_3)_2$	101-102
5	CH_3	CH_2OCH_3	Oil
6	H	$CH(CH_3)_2$	86-88
7	CH_3	$CH_2CH_2CH(CH_3)_2$	92-94
8	C_2H_5	$CH_2CH(CH_3)_2$	68-70
9	CH_3	$CH(CH_3)C_2H_5$	103-109
10	$CH(CH_3)_2$	$CH(CH_3)_2$	106-109
11	CH_3		87-88
12	CH_3	$-CH(SCH_3)-CH_3$	127-129
13	CH_3	CH_3	128-130
14	CH_3	$C(CH_3)_3$	110-115
15	H	C_2H_5	64-66
16	H	$CH_3CH_2CH_3$	66-70
17	CH_3	C_6H_5	148-152
18	CH_3	$CH_2SC_2H_5$	78-82

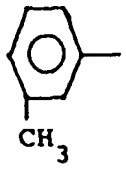
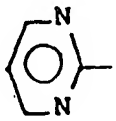
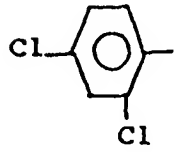
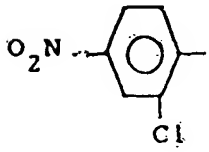
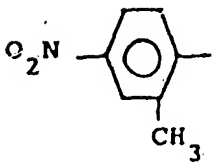
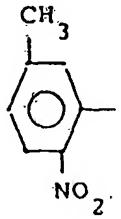
Table V

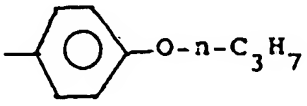
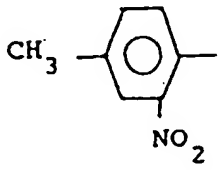
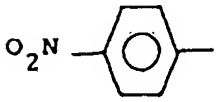
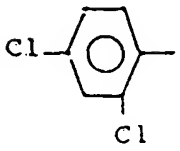
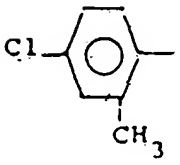
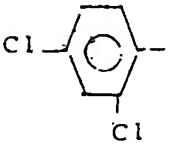
Compounds of formula



No.	Aryl	R_3	M p. [°C]
1		$CH(CH_3)_2$	83-86
2		$CH(CH_3)_2$	74-76
3		$CH(CH_3)_2$	71-75
4		$CH(CH_3)_2$	110-115
5		CH_3	134-137

No.	Aryl	R_3	M p. [°C]
6		$CH(CH_3)_2$	80-82
7		$CH(CH_3)_2$	74-76
8		$CH(CH_3)_2$	134-136
9		$CH(CH_3)_2$	101-105
10		$CH(CH_3)_2$	94-99
11		$C(CH_3)_3$	126-130

No.	Aryl	R_3	M p. [°C]
12		$CH(CH_3)_2$	85-88
13		$CH(CH_3)_2$	170-174
14		C_6H_5	129-145
15		$CH(CH_3)_2$	139-142
16		$CH(CH_3)_2$	124-126
17		$CH(CH_3)_2$	102-104

NO.	Aryl	R_3	Mp. [°C]
18		$CH(CH_3)_2$	78-80
19		$CH(CH_3)_2$	87-92
20		$CH(CH_3)_2$	110-112
21		$CH_2SC_2H_5$	Oil
22			from 112
23			from 112

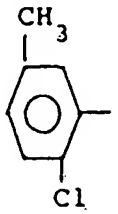
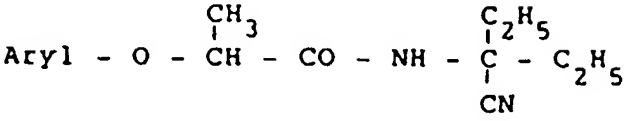
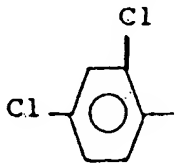
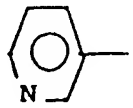
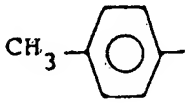
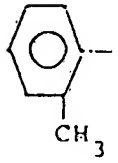
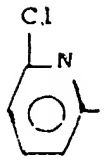
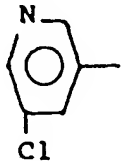
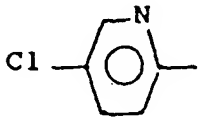
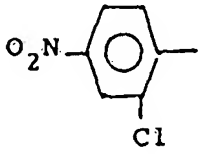
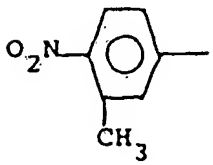
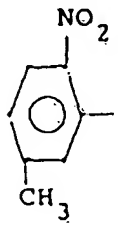
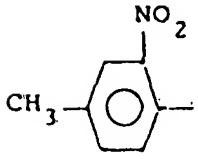
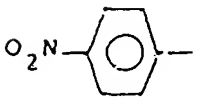
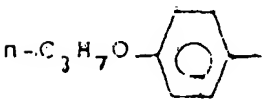
No.	Aryl	R_3	M p.[°C]
24		$CH(CH_3)_2$	69-71

Table VI

Compounds of formula



No.	Aryl	Mp[°C]
1		100-102
2		Oil
3		93-94
4		64-66
5		92-93
6		88-90

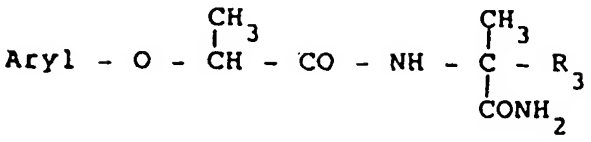
NO.	Aryl	Mp[°C]
7		84-87
8		129-131
9		117-120
10		117-118
11		132-133
12		120-122
13		108-110
14		71 75

45

AT

Table VII

Compounds of formula



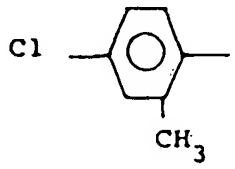
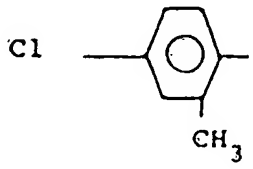
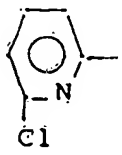
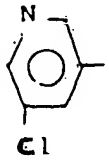
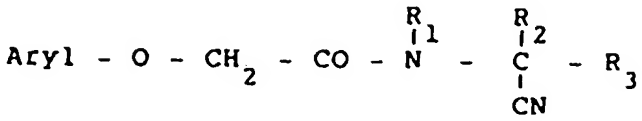
No.	Aryl	R_3	Mp. [°C]
1		$n\text{-}C_3H_7$	100-102
2		$n\text{-}C_3H_7$	108-111
3		$n\text{-}C_3H_7$	111-113
4		$n\text{-}C_3H_7$	115-117

Table VIII

Compounds of formula



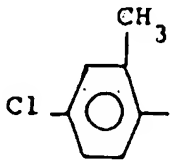
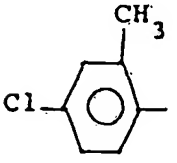
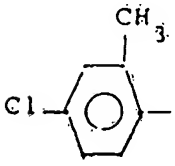
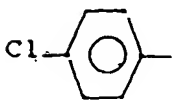
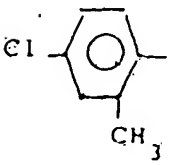
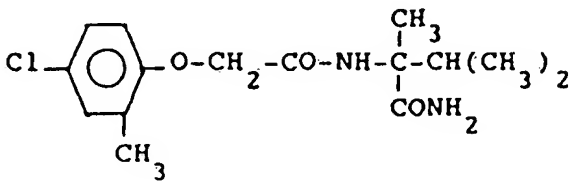
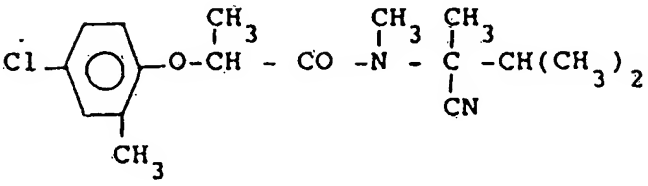
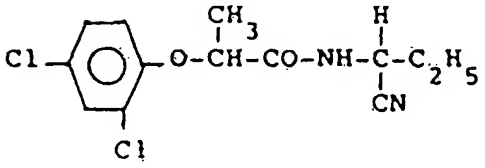
No.	Aryl	R_1	R_2	R_3	M.p. [°C]
1		H	CH_3	$CH(CH_3)_2$	100-103
2		H	C_2H_5	C_2H_5	86-88
3		CH_3	C_2H_5	$CH(CH_3)_2$	Oil
4		H	C_2H_5	C_2H_5	50-52
5		H	CH_3	$n\text{-}C_5H_{11}$	Oil

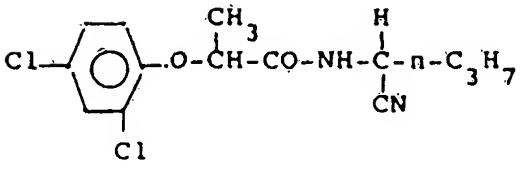
Table IX

Other compounds according to the invention

1  Mp.105-107°C

2  Oil

3  Mp.61-63°C

4  Mp.79-74°C

Examples of formulations:

Example I

Preparation of an emulsifiable concentrate

5.0 parts by weight of active substance according to the invention
3.4 parts by weight of epoxidised vegetable oil
13.4 parts by weight of a combined emulsifier of fatty alcohol polyglycol-ether and calcium alkylaryl-sulphonate
40.0 parts by weight of dimethylformamide
38.2 parts by weight of xylene

The components are mixed together and, for application, diluted with water to give a concentration of active substance of 0.01 to 0.1% by weight.

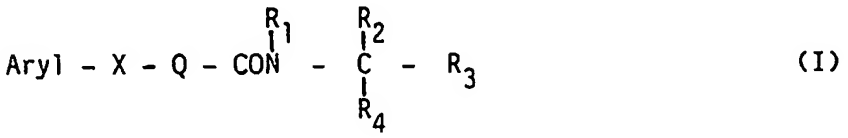
Example II

Preparation of a wettable powder

10 parts by weight of active substance according to the invention
3 parts by weight of sodium fatty alcohol sulphonate
5 parts by weight of salts of naphthalene sulphonic acid-formaldehyde condensate
82 parts by weight of kaolin

The claims defining the invention are as follows:

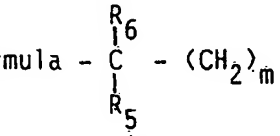
1. A method of preventing or combatting Piricularia in rice plants which comprises the application to said plant of an effective amount of one or more compounds of formula (I)



Aryl - X - Q - CON(R_1) - C(R_2)(R_4) - R_3 (I)

in which

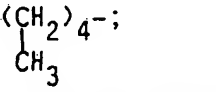
Aryl represents a phenyl group, either unsubstituted or mono- to tri-substituted by C_{1-5} alkyl groups, C_{1-5} alkoxy groups, C_{1-5} alkyl-SO_n groups wherein n represents one of the integers 0, 1 or 2, halogen atoms, groups of formula NO_2, CF_3, CN, CH_3OCH_2, $(CH_3)_2NCH_2$, COOalkyl, $CONH_2$ or phenyl groups; a 1- or 2-naphthyl group; an optionally chlorine-substituted 2-, 3- or 4-pyridyl group; or a pyrimidyl or quinolyl group;

Q represents a group of formula  - $(CH_2)_m$

wherein m is one of the integers 0, 1 and 2;

R_1 represents a hydrogen atom or a C_{1-5} alkyl group or an allyl group,

R_2 and R_3 independently represent hydrogen atoms, C_{1-6} alkyl groups (which may also contain an O or S atom in the chain), C_{3-7} cycloalkyl groups, phenyl groups or groups of formula CH_2-COO-(C_{1-5} alkyl); or

R_2 and R_3 together represent a group of formula $-(CH_2)_4-$, $-(CH_2)_5-$, or  ;

R_4 represent a group of formula CN or $CONH_2$;

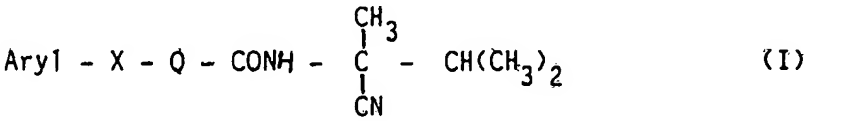
R_5 represents a hydrogen atom or a group of formula CH_3 or C_2H_5;

R_6 represents a hydrogen atom or a group of formula CH_3; and

X represents an oxygen or sulphur atom;

optionally in the form of racemates or mixtures of the optical isomers or in the form of the pure enantiomers or diastereomers.

2. Compounds of formula (I)



Aryl - X - Q - CONH - C(CH_3)(CN) - $CH(CH_3)_2$ (I)

wherein

Aryl represents a phenyl group, either unsubstituted or mono- to tri-substituted by C_{1-5} alkyl groups, C_{1-5} alkoxy groups, C_{1-5} alkyl-SO_n groups wherein n represents one of the integers 0, 1 or 2, halogen atoms, groups of formula NO_2, CF_3, CN, CH_3OCH_2, $(CH_3)_2NCH_2$, COOalkyl, $CONH_2$ or phenyl groups; a 1- or 2-naphthyl group; an optionally chlorine-substituted 2-, 3- or 4-pyridyl group; or a pyrimidyl or quinolyl group;

Q represents a group of formula $-\overset{R_6}{\underset{R_5}{C}}-(CH_2)_m$

wherein m is one of the integers 0, 1 and 2;

R_5 represents a hydrogen atom or a group of formula CH_3 or C_2H_5;

R_6 represents a hydrogen atom or a group of formula CH_3; and

X represents an oxygen or sulphur atom;

optionally in the form of racemates or mixtures of the optical isomers or in the form of the pure enantiomers or diastereomers.

3. Compounds as claimed in claim 2, wherein Aryl is a 4-chlorophenyl, 4-chloro-2-methylphenyl or 2,4-, 3,4- or 3,5-dichlorophenyl group.

4. Compounds as claimed in claim 2 or claim 3, wherein X represents an oxygen atom.

5. Compounds as claimed in any one of claims 2 to 4, wherein Q represents a group of formula $CH(CH_3)$.

6. N-(2-cyano-3-methylbut-2-yl)-2-(4-chloro-2-methylphenoxy)-propamide.

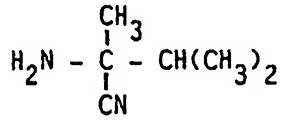
7. A fungicidal composition comprising a compound of formula I as claimed in any one of claims 2 to 6 optionally in the form of racemates or mixtures of the optical isomers or in the form of the pure enantiomers or diastereomers, together with excipients and/or carriers.

8. A process for preparing compounds of formula (I) as defined in any one of claims 2 to 6 wherein

(a) a compound of formula (II)

$$Aryl - X - Q - COY \qquad (II)$$

wherein Aryl, X and Q are as defined in claim 2 and Y represents a leaving group, is reacted with a compound of formula (III)



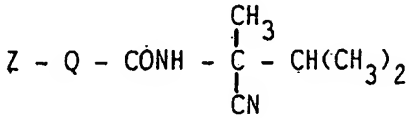
(III)

or

b) a compound of formula (IV)

(IV)

wherein Aryl and X are as defined in claim 2 and M represents a hydrogen atom or an alkali metal cation, is reacted with a compound of formula (V)



(V)

wherein Q is as defined in claim 2 and Z represents a halogen atom or an arylsulphonyloxy group,

and, if desired, mixtures of enantiomers obtained are separated by conventional methods into the individual enantiomers or into pairs of diastereomers.

9. A process for the preparation of a fungicidal composition as defined in claim 7 which comprises admixing one or more compounds of formula (I) as defined in any one of claims 2 to 6 with a carrier and/or excipient.

10. A method of preventing or combatting Pericularia in rice plants which comprises the application to said plants of an effective amount of one or more arylcarboxylic acid derivatives, which derivative is substantially as herein described with reference to any one of Examples 1 to 10 or Table 1 and any one of compounds 1 to 14, Table II and any one of compounds 1 to 66, Table III and any one of compounds 1 to 4, Example IV and any one of compounds 1 to 18, Table V and any one of compounds 1 to 24, Table VI and any one of compounds 1 to 14, Table VII and any one of compounds 1 to 4, Table VIII and any one of compounds 1 to 5 or Table IX and any one of compounds 1 to 4, or a composition comprising said derivative together with a fungicidally acceptable carrier, adjuvant and/or diluent.

11. An arylcarboxylic acid derivative as defined in claim 2, which derivative is as defined herein with reference to any one of Examples 2, 5, 9 or 10 or Table II and any one of compounds 1, 14, 17, 22 to 24, 26 to 30, 33, 36, 39, 44, 46 to 49, 51 to 59 or 66, Table III and compound 1 or 3, Table V and any one of compounds 1 to 4, 6 to 13, 15 to 20 or 24, or Table VIII and compound 1.

12. A fungicidal composition for preventing or combatting Pericularia in rice plants comprising a compound as claimed in claim 11, together with a fungicidally acceptable carrier, adjuvant and/or diluent.

13. A process for preparing an arylcarboxylic acid derivative as defined in claim 2, which process is substantially as herein described with reference to Example 2, 5, 9 or 10.

DATED this NINTH day of JANUARY 1991
Shell Internationale Research Maatschappij B.V.

Patent Attorneys for the Applicant
SPRUSON & FERGUSON

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